KnE Materials Science

TECHNOGEN-2019
IV Congress "Fundamental research and applied developing of recycling and utilization processes of technogenic formations"
Volume 2020

Knowledge E
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Conference Paper

Opening of Nitride Spent Nuclear Fuel

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Abstract

Nitride nuclear fuel (UN + 10-20% PuN) is considered a promising alternative to the widely used oxide nuclear fuel (UO_2). Thermal conductivity and density of nitride fuel are ~ 7 times and 1.3 times higher than that of oxide fuel, respectively. Nitride fuel demonstrates a good compatibility with the cladding of fuel rods made of stainless steel. Along with the development of new fuel, methods for its subsequent processing are being developed. Various options for the initial opening of nitride spent nuclear fuel (SNF) are considered in this article. The use of gaseous chlorine is technologically inconvenient and dangerous when working with radioactive substances. The electrochemical dissolution of nitride SNF cannot be realized due to the formation of a by-product - UNCl. Uranium nitride chloride is an insulator and it blocks the electrochemical process. It was found that the chlorination of nitride SNF with cadmium or lead chlorides makes it possible to carry out 100% UN → UCl_3 conversion. The use of voloxidation (oxidation of nitride SNF to oxides) as the first stage of processing will make the entire technology universal, suitable for processing both nitride and oxide SNF. The choice of the method for opening SNF depends on the choice of the subsequent stages of its processing.

Keywords: nitride spent nuclear fuel, SNF, chlorination, anodic dissolution, UNCl, "soft" chlorination, voloxidation, processing

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Published: 31 December 2020

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the TECHNOGEN-2019 Conference Committee.

1. Introduction

Currently, most light water reactors and fast neutron reactors use uranium dioxide, UO_2, as fuel [1]. It has a high melting point (~ 2800 °C) and it has a high chemical resistance. At the same time, it has low thermal conductivity and low density of heavy nuclei (uranium). To avoid these shortcomings, a search for a new improved fuel is underway. Dense nitride fuel is the most promising candidate. Comparative characteristics of several types of fuel are given in Table 1.

UN has the best characteristics considering the common value of the properties analyzed. In terms of thermal conductivity and content of heavy nuclei, UN is inferior only to metallic uranium. High thermal conductivity allows reducing the temperature

of the fuel to 450 - 500 ˚C [1], against ~ 2000 ˚C for UO_2. The presence of porosity allows one to compensate the swelling of the fuel. Along with the development of fuel fabrication methods, the methods for reprocessing nitride spent nuclear fuel (SNF) are being developed. A solid solution of UN + 15- 20% PuN is the most likely composition of nitride fuel. In this report, we consider possible methods for opening nitride SNF to dissolve it in the molten LiCl-KCl eutectic.

Table 1: Some thermophysical characteristics of various types of fuel [1].

Property	UO_2	UC	UN	U
Theoretical density and density of heavy nuclei	11.0 / 9.9	13.6 / 12.9	14.3 / 13.5	19.0 / 19.0
Melting point, t_m, ˚C	2850	~2350	2805	1135
Thermal conductivity, W/(m·K)	2.7	17.0	18.0	20.0
Heat of fusion, kJ/mol	277	186	170	38.0
Coefficient of linear thermal expansion, 10^{-6}/K	11	11	10	18

2. Chlorination with chlorine gas

The reactions of UN chlorination by gaseous chlorine have large negative values of Gibbs energy changes, see reactions (1) and (2).

$$UN + 1.5Cl_2 = UCl_3 + 0.5N_2\uparrow \qquad \Delta G = -466 \text{ kJ/mol at } 500\ ^\circ C \tag{1}$$

$$UN + 2Cl_2 = UCl_4 + 0.5N_2\uparrow \qquad \Delta G = -567 \text{ kJ/mol at } 500\ ^\circ C \tag{2}$$

According to the thermodynamic modeling results (see Figure 1), the interaction of UN + Cl_2 proceeds in a series of parallel reactions, through the formation of UNCl and various nitrides ($UN_{1.69}$, UN_2). At the molar ratio of Cl_2 / UN ≈ 1.7, no intermediate products remain, and the mixture of UCl_3 + UCl_4 composition is formed. At the molar ratio of Cl_2/UN ≈ 2 and more, a part of UCl_4 is chlorinated to UCl_5, $(UCl_5)_{2(gas)}$, $UCl_{6(gas)}$. The use of gaseous chlorine is technologically inconvenient, especially when working with radioactive substances. Therefore, we consider other methods of primary opening.

3. Anodic dissolution

Uranium mononitride has electronic conductivity; its electrical conductivity is comparable to that of graphite. Therefore, it seems attractive to transfer it into a solution by anodic dissolution:

$$UN - 3e = U^{3+} + 0.5N_2\uparrow \tag{3}$$

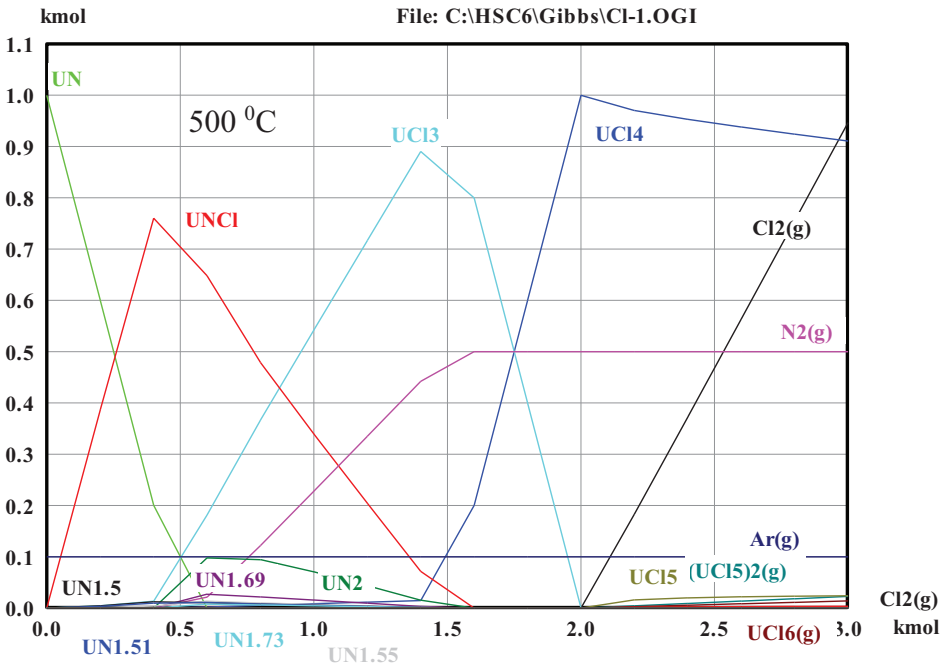

Figure 1: Equilibrium composition of the UN + Cl_2 reaction products. Our data.

When using a liquid cadmium cathode, it is convenient to add a certain amount of $CdCl_2$ to the melt in order to prevent the release of alkali metal at the cathode. Then the following reaction at the cathode takes place:

$$Cd^{2+} + 2e = Cd\downarrow \quad (4)$$

A series of experiments was conducted. The results of one of the experiments are shown in Figure 2. It was found that after the dissolution of a certain amount of UN, the process slows

down and actually stops. This is due to the formation at the UN surface of non-conductive uranium nitride chloride, UNCl, which passivates the anode. A tendency that the current efficiency decreases as the current density increases and vice versa was found. It is likely that at an anode current density of ~ 1 mA/cm^2 or less, the passivation does not occur. The same behavior was noted in [2]. At the cathodic potential more negative than -0.55 V against Ag^+/ Ag (1 wt.% AgCl) (-1.755 B against Cl_2/Cl^-), UNCl is not formed. But such values of current density are too low for technological applications. Currently, these experiments are suspended and efforts are focused on chlorination using 3*d*-metal chlorides as chlorinating agents.

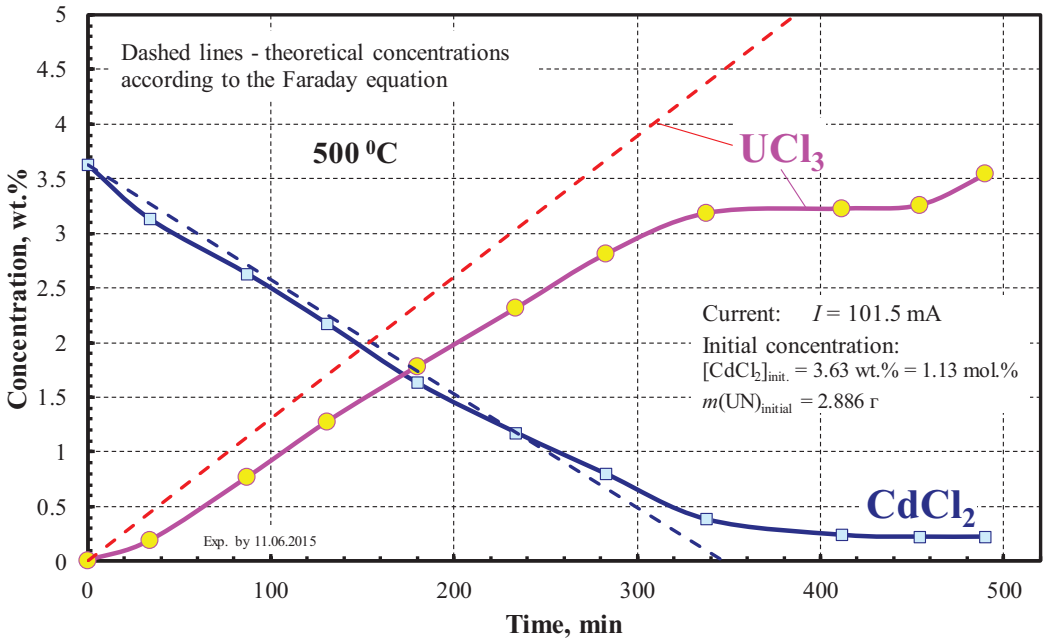

Figure 2: Kinetics of UN anodic dissolution in the LiCl-KCl melt + 1 mol.% $CdCl_2$. Our data.

4. ``Soft'' Chlorination

By “soft” chlorination we refer to chlorination without the use of gaseous Cl_2. Instead of chlorine gas, it is proposed to use 3*d*-metal ions as chlorinating agents. For example, Zn^{2+}, Cd^{2+}, Pb^{2+} or Bi^{3+} [3, 4].

Currently, $CdCl_2$ and $PbCl_2$ are considered as the most promising chlorinating agents. The chlorination reactions and the change in Gibbs energy during these reactions at 500 °C are presented below:

$$UN + 1.5CdCl_2 = UCl_3 + 1.5Cd + 0.5N_2\uparrow \quad \Delta G = -59.8 \text{ kJ/mol} \tag{5}$$

$$PuN + 1.5CdCl_2 = PuCl_3 + 1.5Cd + 0.5N_2\uparrow \quad \Delta G = -149 \text{ kJ/mol} \tag{6}$$

$$UN + 1.5PbCl_2 = UCl_3 + 1.5Pb + 0.5N_2\uparrow \quad \Delta G = -98.0 \text{ kJ/mol} \tag{7}$$

$$PuN + 1.5PbCl_2 = PuCl_3 + 1.5Pb + 0.5N_2\uparrow \quad \Delta G = -187 \text{ kJ/mol} \tag{8}$$

However, experiments revealed significant problems. At the interaction of UN + $CdCl_2$ in the molten LiCl-KCl eutectic at 500 ^{0}C, only ~30% of UN was converted to UCl_3. The rest of uranium formed a dark precipitate, which consisted of a mixture of $UN_{1.5}$, U_4N_7, UN_2 and UNCl according to the X-ray phase analysis data. To find the conditions providing 100% UN → UCl_3 conversion, we performed thermodynamic modeling using the HSC Chemistry program. This simulation made it possible to understand what was happening at 500 °C and to find a solution to the problem. One kilomol of UN was titrated with cadmium chloride. The process proceeded in the molten LiCl-KCl eutectic;

therefore, the activity coefficients of dissolved substances were also taken into account. The simulation results at 500 °C are shown in Figure 3. Modeling showed that, indeed, at 500 °C the UN → UCl_3 conversion is only about 30%. In addition to the above phases, the precipitate may also contain phases $UN_{1.51}$, $UN_{1.55}$, $UN_{1.59}$, $UN_{1.69}$, which were not detected by XRF. It was found that as the $CdCl_2$/UN molar ratio increases, the chlorination degree increases and it can reach ~ 50% at $CdCl_2$ / UN = 15. Apparently, at 500 °C, the 100% UN → UCl_3 conversion is not reachable at all. It was also found that with increasing temperature, the chlorination degree increases and reaches 100% at 750 °C. The reaction also proceeds through the formation of a series of intermediate nitrides, but all of them are chlorinated to UCl_3 with a small, ~ 20%, excess of $CdCl_2$. The experiment fully confirmed this conclusion. Pure pinkish-violet salt smelts of LiCl-KCl + UCl_3 without any other inclusions except residual $CdCl_2$ were obtained. Easy distillation of the formed cadmium metal is the advantage of $CdCl_2$ application, and the high process temperature (750 °C) is the disadvantage.

A comparison of equations (5) - (6) and (7) - (8) demonstrates that $PbCl_2$ is a more powerful chlorinating agent than $CdCl_2$. Its use allowed to reduce the chlorination temperature to 650 °C while maintaining 100% UN → UCl_3 conversion. This conclusion is confirmed experimentally. Modeling also shows that chlorination also proceeds through the stage of formation of a number of stoichiometric and non-stoichiometric nitrides and UNCl, which then dissolve in excess $PbCl_2$. A decrease in the reaction temperature is a positive moment, but lead, as opposed to cadmium, does not distill off at such temperatures (P(Pb) ≈ 0.2 Pa at 650 °C). However, potentially lead has another advantage. In real SNF, noble metals Ru, Rh, Pd are formed. It is very likely that the lead formed will accumulate noble metals and, maybe, also Ag, Mo and Tc. By removing a lead ingot, we will remove up to 40% of activity at the first stage.

5. Voloxidation

Here, by voloxidation, we refer to the oxidation of nitride SNF to oxides. The use of voloxidation at the first stage will make the SNF reprocessing scheme universal, i.e. suitable both for nitride and for oxide fuels. At the voloxidation stage, it will be possible to get rid of a number of volatile components of SNF - Xe, Kr, N_2, Cs and a number of others, depending on the temperature and the oxidizing gas. In Figures 4 and 5 the equilibrium SNF compositions formed under different modes of voloxidation are shown.

As can be seen from Figures 4 and 5, UN is initially oxidized to UO_2, but in excess air it can be oxidized further to U_3O_7, U_3O_8, UO_3. Plutonium nitride is oxidized to PuO_2. Molybdenum goes through the chain of transformations Mo → $MoN_{0.5}$ → Mo → MoO_2 →

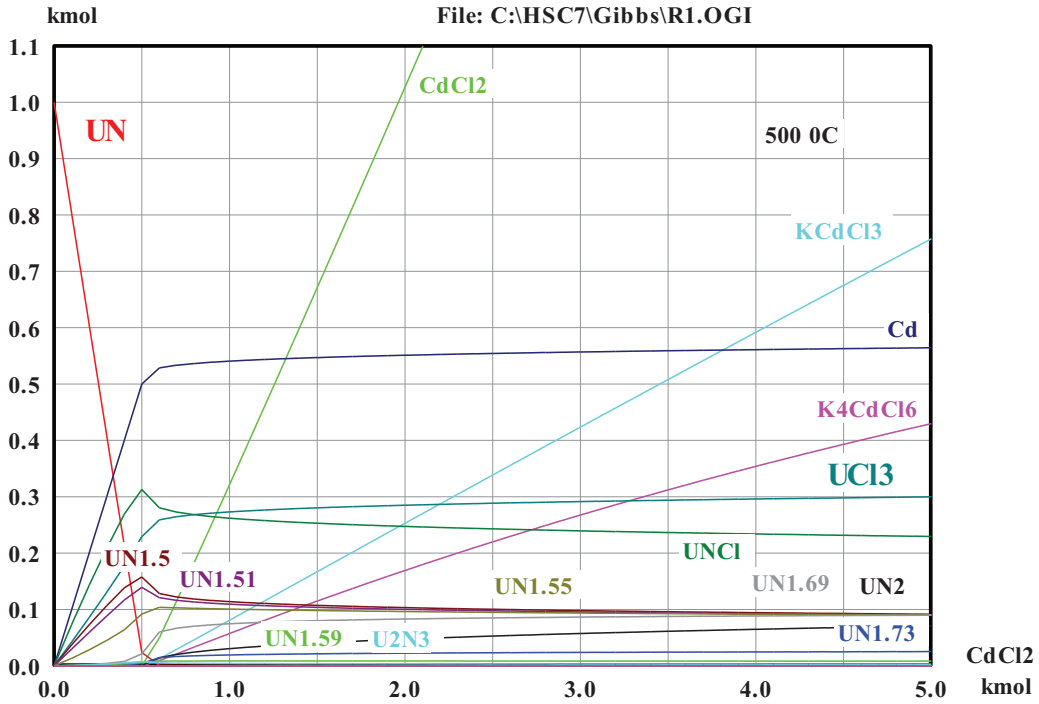

Figure 3: Equilibrium composition of the UN - $CdCl_2$ system in the eutectic LiCl-KCl melt at 500 ^{0}C according to the thermodynamic simulation. Our data.

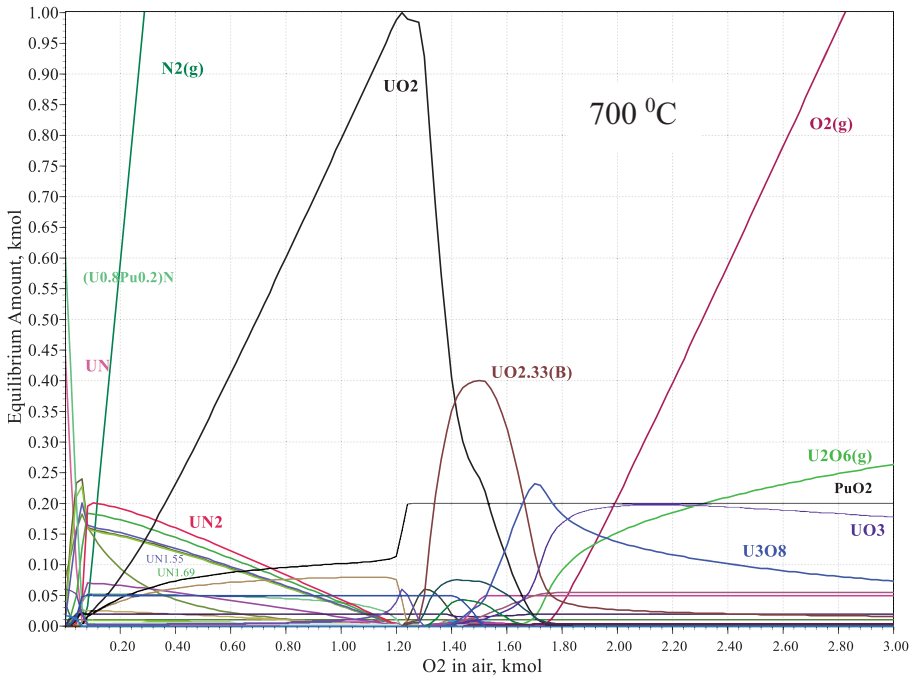

Figure 4: Equilibrium composition of oxidation products of model SNF by air. The initial composition of the model SNF is UN + 0.2PuN + 0.06Mo + 0.05Ru + 0.04NdN, kmol. Our data.

$UMoO_6$ (mixed with UO_2MoO_4). Ruthenium is most resistant to oxidation. But in excess air, even ruthenium oxidizes to RuO_2. Neodymium nitride is oxidized to Nd_2O_3.

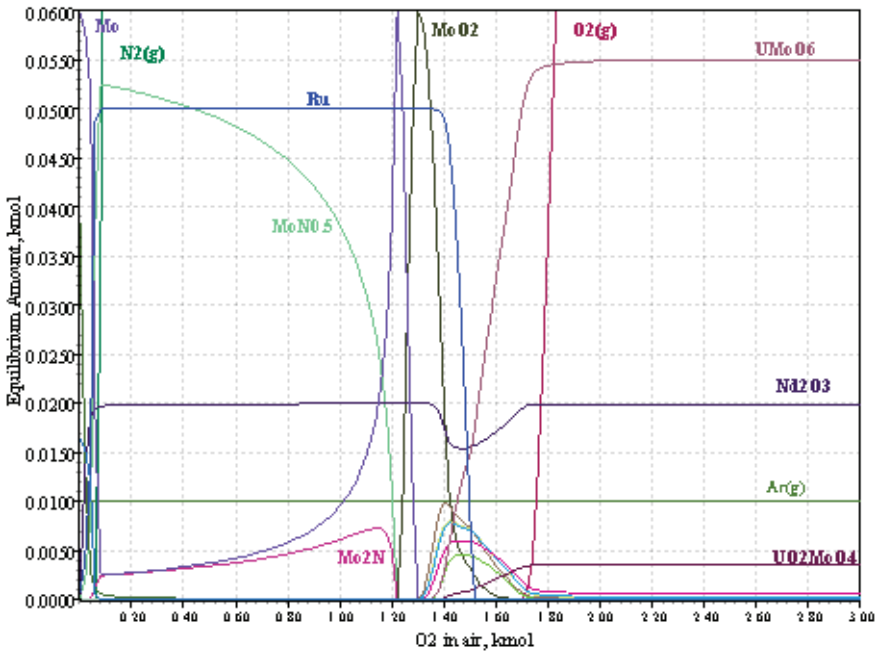

Figure 5: Same as Figure 4, only the ordinate axis is limited to 0.06 kmol, so that the equilibrium compositions of substances containing Mo, Ru, and Nd become visible. Our data.

6. Conclusion

Various methods for the initial opening of nitride SNF are briefly reviewed. The choice of the method for the first stage depends on its applicability in the full SNF reprocessing scheme.

References

[1] Shimkevich, A., Proshkin, A. and Sedov, A. (2011). Through Innovation. Promising Dense Fuel For Power Reactors. *ROSENERGOATOM*, issue 10, pp. 36-41.

[2] Shirai, O., *et al*. (2002). Recovery of U by electrolysis of UN in LiCl-KCl Eutectic Melts. *Journal of Nuclear Science and Technology* Vol. 39, *Suppl. 3,* pp. 745-748.

[3] Zaykov, Y. P., *et al*. (2017, June). Pyrochemical Recycling of the Nitride SNF of Fast Neutron Reactors in Molten Salts as a Part of the Short-Circuited Nuclear Fuel Cycle. Presented at *Int. Conf. on Fast Reactors and Related Fuel Cycles: Next Generation Nuclear Systems for Sustainable Development 2017 (FR17)*, *Yekaterinburg, Russia*. Vienna, Austria: International Atomic Energy Agency (IAEA), 262 p.

[4] Shishkin, V. Y., *et al*. (2017, September). The Peculiarities of Pyrochemical Reprocessing of Spent Nuclear Fuel. Presented at *GLOBAL 2017 Int. Nuclear Fuel Cycle Conf., Seoul, Republic of Korea*. Proceedings, Publication of works online: Paper EA-104, p. 3. Retrieved from http://www.global2017.org/congress/index2.php